



Using a multi-dimensional approach for catchment scale herbicide pollution assessments

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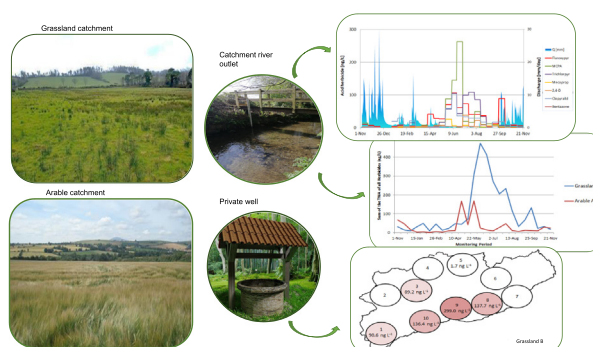
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HIGHLIGHTS

- Acid herbicides were detected in both stream and ground water of two agricultural catchments.
- Herbicides were present in the streams all year: concentrations peaked in summer and loads in winter.
- Herbicides were detected in 38% of surveyed drinking water wells, some exceeding recommendations.
- Hydrological controls played a large role on the occurrence of when and where herbicide were present.
- Targeted mitigation measures that consider hydrological risky areas and times are recommended.

GRAPHICAL ABSTRACT



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ABSTRACT

Worldwide herbicide use in agriculture, whilst safeguarding yields also presents water quality issues. Controlling factors in agricultural catchments include both static and dynamic parameters. The present study investigated the occurrence of herbicides in streams and groundwater in two meso-scale catchments with contrasting flow controls and agricultural landuse (grassland and arable land). Using a multi-dimensional approach, streams were monitored from November 2018 to November 2019 using Chemcatcher® passive sampling devices and groundwater was sampled in 95 private drinking water wells. The concentrations of herbicides were larger in the stream of the *Grassland catchment* (8.9–472.6 ng L⁻¹) dominated by poorly drained soils than in the *Arable catchment* (0.9–169.1 ng L⁻¹) dominated by well-drained soils. Incidental losses of herbicides during time of application and low flows in summer caused concentrations of MCPA, Fluroxypyr, Trichlorpyr, Clopyralid and Mecoprop to exceed the European Union (EU) drinking water standard due to a lack of dilution. Herbicides were present in the stream throughout the year and the total mass load was higher in winter flows, suggesting a persistence of primary chemical residues in soil and sub-surface environments and restricted degradation. Losses of herbicides to the streams were source limited and influenced by hydrological conditions. Herbicides were detected in 38% of surveyed drinking water wells. While most areas had concentrations below the EU drinking water standard some areas with well-drained soils in the *Grassland catchment*, had concentrations exceeding recommendations. Individual wells had concentrations of Clopyralid (619 ng L⁻¹) and Trichlorpyr (650 ng L⁻¹). Despite the study areas not usually associated with herbicide pollution, and annual mass loads being

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comparatively low, many herbicides were present in both surface and groundwater, sometimes above the recommendations for drinking water. This whole catchment assessment provides a basis to develop collaborative measures to mitigate pollution of water by herbicides.

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1. Introduction

Pesticides play a vital role in maximising production in modern agriculture and have been used widely since the 1940s (Bolognesi and Merlo, 2019; Chormey et al., 2020). However, despite national and international regulations, continued use and intensive applications of pesticides to agricultural land each year have resulted in their widespread distribution in the environment (Huber et al., 2000; Herrero-Hernández et al., 2013; McManus et al., 2017; Cui et al., 2020; de Souza et al., 2020; Villamizar et al., 2020). This may cause high residual levels of pesticides in soil and a small proportion can potentially contaminate surface and groundwater resources (Pullan et al., 2016). This diffuse source contamination can impact the chemical and ecological status of surface water and groundwater and can also present compliance problems for water supply companies if the water is abstracted for drinking purposes (Bach et al., 2001; Brown et al., 2004; Gregoire et al., 2009; Szekacs et al., 2015; Wang et al., 2019). For mitigation and management it is important to identify critical source areas and times of pesticide usage coinciding with hydrologically sensitive areas and periods. For the protection of water resources, the natural environment and human health (Fernandez et al., 2014; Zhang et al., 2016), there is a need to understand the driving processes that trigger and control the transport of pesticides from soil to water resources to inform and update best management practices and mitigation measures to reduce such losses. Monitoring of pesticides at the catchment-scale provides highly valuable data for their management and the composition and levels of pesticides in surface and groundwater can reflect hydrology and dominant flow paths within the catchment (Cui et al., 2020). For example, transport of pesticides from agricultural fields to neighbouring surface water bodies can be facilitated along surface (Lefrancq et al., 2017; Sandin et al., 2018; Zhang et al., 2018), shallow subsurface runoff through tile drains (Brown and van Beinum, 2009), or deeper vertical movement to connected groundwater (Demir et al., 2019; Swartjes and Van der Aa, 2020). Such losses are also influenced by static and dynamic factors such as the physico-chemical characteristics of soil-subsoil-bedrock continuum and pesticide itself, by landuse, management practices, and, the timing of pesticide application (Holvoet et al., 2007; Arias-Estévez et al., 2008; Morton et al., 2019; Villamizar et al., 2020). Other factors include prevailing environmental conditions such as high temporal variability in rainfall events after application (Brown et al., 1995; Schulz, 2004).

Recent studies have reported the presence of pesticides in both surface and groundwater receptors in most of the European countries (e.g. Sattler et al., 2007; Shriks et al., 2010; Evans, 2009; Tediosi et al., 2012; Tediosi et al., 2013; McManus et al., 2014; McManus et al., 2017; Kapsi et al., 2019), in the USA (Stone et al., 2014; Gliniski et al., 2018; Battaglin et al., 2016), Canada (Metcalf et al., 2019; Montiel-León et al., 2019) and China (Brauns et al., 2018; Sun et al., 2018). These data can infer processes but are also used to report exceedances of pesticide contaminants above the permissible limits determined under national and international regulations. In the UK, for example, pesticide monitoring programmes in surface and groundwater bodies carried out since 1985 and other research studies have reported the occurrence and distribution in these natural systems (Croll, 1991; Skinner et al., 1997; Bloomfield et al., 2006; Loos et al., 2009; Gillman et al., 2012; Bloodworth et al., 2014; Zhang et al., 2016; Cui et al., 2020). Similar studies have also shown how this presence may pose problems for environmental agencies and water supply companies to comply with drinking water quality standards (Evans, 2009; Tediosi et al., 2012).

Pesticide monitoring of rivers in the USA between 1992 and 2011 reported the exceedance of one or more pesticides above the admissible limits in agricultural catchments (Stone et al., 2014). Monitoring programs across Europe have also demonstrated the presence of various pesticides in rivers, lakes and subsurface waters that may additionally pose potential ecological risks to aquatic species (Brown and van Beinum, 2009; Loos et al., 2009; Proia et al., 2013).

In the European Union (EU), precautionary limits of $0.1 \mu\text{g L}^{-1}$ for a single pesticide and $0.5 \mu\text{g L}^{-1}$ for the sum total of pesticides in drinking water were first established in the Drinking Water Directive (80/778/EEC) in 1980 (EC, 1980). These regulations were further strengthened by the introduction of the EU Water Framework Directive (2000/60/EC) in 2000 and Groundwater Directive (2006/118/EC) in 2006 which required member states to continuously monitor the levels of organic pollutants in surface and groundwater bodies and to take measures to maintain required standards for drinking water (EC, 2000, 2006).

Ireland has an agricultural economy ranging from intensive to extensive and marginal with 53% of land used for agriculture, mostly grassland (93%) but with significantly productive arable and horticultural enterprises (7%) (Clagnan et al., 2018). Agrochemicals are intensively applied to arable field and grasslands but, beyond statutory reporting, approaches to reporting the occurrence and distribution of pesticides residues and their metabolites in Irish soils and waters has been limited to single water body receptors and not integrated to catchment processes (McGrath, 1995; Piwowarczyk and Holden, 2012; McManus et al., 2014; McManus et al., 2017). For example, a groundwater monitoring study by McManus et al. (2014) reported the occurrence of pesticide active substances in 27% of the samples out of 845, where some samples had at least one detection greater than (or equal to) the drinking water limit of $0.1 \mu\text{g L}^{-1}$. They also reported that the herbicides Mecoprop, 2-Methyl-4-Chlorophenoxyacetic Acid (MCPA), Lindane, Glyphosate, Atrazine and 2,4-D were the most frequently detected pesticides in water samples.

MCPA is of particular importance in Irish agriculture due to its frequent and high usage and the frequency of detection by statutory monitoring has increased in recent years (Morton et al., 2019). MCPA is a selective acid herbicide mostly used to reduce and inhibit rush (*Juncus* spp.) cover on grasslands and certain broadleaf weed species. The compound is highly mobile in soils due to its high water solubility and relatively low soil adsorption (Koc), and is highly susceptible to contaminate surface and groundwater. Morton et al. (2019), focussing on MCPA, suggested that to develop better risk assessments there was a need to increase the empirical evidence base for pesticide transfers from land to water and to further inform on links to hydrometeorological drivers and vulnerable times.

The present study builds on these recommendations with the aim of developing a highly empirical and integrated assessment of herbicide drivers, conditions and transfers across surface waters and groundwaters, in grassland and arable landuse settings, within distinct lithological settings and across hydrometeorological seasons. The main objectives of the study were to: (1) build a detailed four dimensional dataset of herbicide concentrations in river catchments with contrasting hydrology and agricultural landuse, and; (2) use these data to reassess vulnerability to herbicide contamination to water both spatially and temporally. This is an important development for integrated assessments wherever herbicides are used and, in Ireland, recognises the important role both groundwater and surface water has for intrinsic ecological health and also as important region specific source drinking water supplies.

2. Material and methods

2.1. Site description

The monitoring was carried out in two hydro-geologically distinct meso-scale catchments located in the south-east of Ireland in County Wexford (Fig. 1, Table 1). These catchments are part of a long-term observatory network described in detail elsewhere (Fealy et al., 2010; Wall et al., 2011). In summary, both catchments are intensively farmed but with different agricultural landuses; one is dominated by arable crop production and the other is dominated by grassland. The catchments are in close proximity (ca. 20 km) and have a temperate maritime climate with an average rainfall of 1024 mm year⁻¹ (2010–2019). Henceforth, the two catchments will be referred to by their dominating landuses.

The *Grassland catchment* is 12 km² with 97% of the land used for agricultural production. Approximately 78% of the agricultural land is used for grass production (mainly dairy, beef and sheep) and 20% is used for arable crops (mainly spring barley). The catchment has 74% poorly drained Gley soils in the lowland and 26% well drained Brown earths soils in the uplands. Due to poor soil drainage, quick surface pathways dominate hydrological storm hydrology (Mellander et al., 2015) and the losses of herbicides are expected to be mostly via overland flow to surface water. Although, grassland typically does not routinely receive herbicide applications it is common with weed control using a small range of selective and broad-spectrum herbicides. The most frequently used acidic herbicides under grassland agriculture in Ireland include MCPA, Trichloropyr, Fluroxypyr, Clopyralid, Mecoprop, 2,4-D and Dicamba.

The *Arable catchment* is 11 km² with 93% of the total land used for agricultural production. The arable land represents about 54% (mainly spring barley and winter wheat) of the catchment area and the remaining is grassland, mainly for dairy and beef cattle. This catchment is dominated by well-drained acid Brown Earth soils (80% Cambisols), and poorly drained Gley soils make up most of the remainder. Due to the well-drained nature of the soils the dominating hydrological pathways

Table 1

Main physical and hydrological characteristics and land use patterns of the Grassland and Arable catchment.

Properties	Grassland catchment	Arable catchment
Total area	11.9 km ²	11.2 km ²
Altitudinal range	20–230 m a.s.l.	20–210 m a.s.l.
Land use split	Grassland 78%, Arable 20%, 2% other	Arable 54%, Grassland & Non-agricultural uses 39%, other 7%
Farming enterprise	Dairying/sheep/beef production/Sports horses, Spring barley/other cereals	Spring barley/winter barley/oil-seed rape/potatoes Sheep/beef production
Soil group	Poorly drained gley 74%, well drained brown earth 26%	Well drained brown earth 80%, poorly drained gley 20%
Geology	Permeable fractured rhyolitic volcanic and slate	2–20 m layer of highly permeable weathered slate overlying fresh slate and siltstone
Hydrological flow pathways	Surface pathways dominating	Subsurface pathways dominating
Annual rainfall, 2019 (2009–2019)	1030 mm (1037 mm)	1110 mm (1012 mm)
River discharge, 2019 (2009–2019)	555 mm (496 mm)	668 mm (548 mm)

are belowground (Mellander et al., 2015) and loss of herbicides to surface water is expected to be mostly via ground water. There may also be herbicides transferred via surface pathways during larger rain events, and especially when soils are already saturated. Herbicides and fungicides associated with arable production of spring barley in Ireland are Fluroxypyr, Mecoprop, Chlorothalonil, Prothioconazole, Fenpropimorph and are applied on crops in early to mid-growing season from April to May. The grassland in the *Arable catchment* receives some herbicide application to control grassland weeds and this is mainly by MCPA

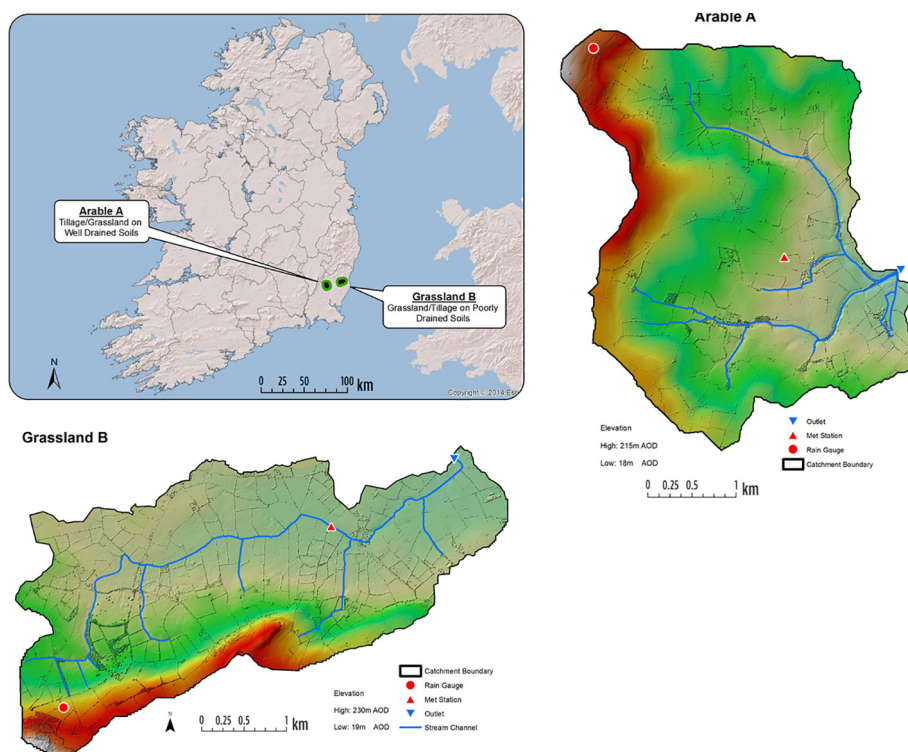


Fig. 1. a) Map of Ireland and location of the *Grassland catchment* and *Arable catchment*; b) river networks, locations of catchment outlets, meteorological stations and rain gauges in the *Grassland catchment*, and c) in the *Arable catchment*.

application. The physico-chemical properties of the studied herbicides are given in Table 2.

Both surface waters and groundwater were monitored in this study – the former in catchment streams and the latter in private groundwater wells used as source drinking water.

2.2. Hydrometric data

Meteorological and hydrological data were collected as part of the long term catchment observatory network since 2009. Standard weather parameters such as rainfall, air temperature, relative air humidity, solar radiation and wind speed were collected on a 10-minute basis using a weather station (BWS200, Campbell Scientific) in the central lowlands of each catchment. In both catchments, stream discharge was calculated from the water levels recorded every 10-minutes with OTT Orpheus Mini vented-pressure instruments installed in stilling wells at the catchment outlets. The velocity-area method, using OTT Acoustic Doppler Current meters, was used to develop rating curves on Corbett flat-v non-standard weirs and used to convert the monitored water level to discharge.

2.3. Surface water sampling

Monitoring of herbicide concentrations in surface water was carried out using Chemcatcher® passive sampling devices (T.E. Laboratories

Ltd.) that effectively concentrate the pollutant onto the receiving disk over deployment periods. A suite of 18 herbicides was monitored (Table 2). Samplers were installed in streams at the outlets of the two catchments at the start of November 2018, deployed and removed on a fortnightly basis to provide a time weighted average concentration. Chemcatchers® have been used previously in herbicide monitoring studies and preferred to discrete grab sampling in dynamic river systems where highly mobile herbicide concentrations can rapidly change (Schäfer et al., 2008; Münze et al., 2015; Novic et al., 2017; Townsend et al., 2018). The Chemcatchers® used in this monitoring study were 47 mm in diameter and consisted of five main components; a supporting disk, receiving disk, diffusion limiting membrane, retaining ring, and transport lid. The preparation of Chemcatchers® for deployment was performed by T.E. Laboratories Ltd. following a procedure described in Townsend et al. (2018).

Briefly, all PTFE (Polytetrafluoroethylene) parts of the sampler were soaked overnight in a 2–5% Decon 90 detergent, rinsed with deionised water followed by a wash with acetone in an ultrasonic bath for 10 min and dried. Circular polyethersulfone (PES) membranes (Supor 200 membrane, 0.2 µm pore size, 50 mm diameter) were soaked in methanol for 24 h and then rinsed thoroughly with deionised water and allowed to dry before use. Receiving phase Anion-SR (poly(styrenedivinylbenzene)copolymer) disks (used for retaining acidic herbicides) were conditioned using a vacuum manifold with 50 mL each of acetone and methanol followed by 50 mL of deionised water

Table 2
Key physicochemical properties of the studied herbicides (Source: pesticide properties database, University of Hertfordshire, UK. Available at: <http://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm>).

Herbicide	CAS name	Water solubility (mg L ⁻¹ , 20 °C)	K _{ow} (Log P, 20 °C)	K _{oc} /K _{foc} (mL g ⁻¹)	Soil degradation, DT ₅₀ * Field (days)	Aqueous hydrolysis, DT ₅₀ (Days)	Photostability in water (DT ₅₀ in days)	Usage
Clopyralid	3,6-dichloro-2-pyridinecarboxylic acid	7850	−2.63	5.0	8.2	Stable	271	Post-emergence control of many broad-leaved weeds in a range of crops
Picloram	4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid	560	−1.92	13	–	Stable	2.0	Control of broad-leaved weeds on non-crop and utility areas
2,3,6-TBA	2,3,6-trichlorobenzoic acid	7700	2.71	65	–	–	Stable	Post-emergence control of annual & perennial broad-leaved weeds
Dicamba	3,6-dichloro-2-methoxybenzoic acid	250,000	−1.88	12.36**	3.98	Stable	50.3	Control of annual & perennial broad-leaved weeds & brush species
Benazolin	4-chloro-2-oxo-3(2H)-benzothiazoleacetic acid	500	1.34	36	21	Stable	Stable	Post-emergence control of broad-leaved weeds
Fluroxypyr	((4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy)acetic acid	6550	0.04	68**	51	223	stable	Post-emergence control of annual & perennial broad-leaved weeds
Bentazone	3-(1-methylethyl)-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide	7112	−0.46	55.3	7.5	Stable	–	Post-emergence control of annual weeds in a variety of crops
Bromoxynil	3,5-dibromo-4-hydroxybenzonitrile	38,000	0.27	302	8	Stable	0.5	Post-emergence control of annual broad-leaved weeds
2,4-D	(2,4-dichlorophenoxy)acetic acid	24,300	−0.82	39.3	28.8	Stable	38	Control of broad-leaved weeds in arable & grassland
MCPA	(4-chloro-2-methylphenoxy)acetic acid	29,390	−0.81	74**	25	Stable	0.05	Control of annual & perennial broad-leaved weeds mostly in grassland agriculture
Trichlorpyr	((3,5,6-trichloro-2-pyridinyl)oxy)acetic acid	8100	−0.45	27	30	8.7	0.1	Control of broad-leaved & woody weeds on uncultivated areas
Ioxynil	4-hydroxy-3,5-diiodobenzonitrile	3034	2.2	303**	5	Stable	5	Post-emergence control of annual broad-leaved weeds
Dichlorprop	2-(2,4-dichlorophenoxy)propanoic acid	350	2.29	74	10	Stable	–	Post-emergence control of annual & perennial broad-leaved weeds
2,4,5-T	2,4,5-trichlorophenoxyacetic acid	268	4.0	10	–	–	–	Used on non-crop areas i.e. grass pastures, farmyards, ditchbanks and roadways
Mecoprop	2-(4-chloro-2-methylphenoxy)propanoic acid	250,000	−0.19	47	8.	Stable	44]	Post-emergence control of broad-leaved on non-crop areas
2,4-dB	4-(2,4-dichlorophenoxy)butanoic acid	4385	1.22	224	15.6	Stable	17.2	Post-emergence control of annual & perennial broad-leaved weeds
MCPB	4-(4-chloro-2-methylphenoxy)butanoic acid	4400	1.32	108**	7	Stable	2.6	Post-emergence control of annual & perennial broad-leaved weeds
Fenoprop	2-(2,4,5-trichlorophenoxy)propanoic acid	140	3.8	2600	14	–	–	Control of woody plants and broad leaved weeds

*DT₅₀ (Time for pesticide concentration to decrease 50%) classification from European Union (EU) dossier laboratory studies, ** K_{foc} (Freundlich organic carbon sorption coefficient).

and then 50 mL each of sodium hydroxide and deionised water. Once the conditioning was complete, all parts of the Chemcatchers® were carefully assembled and a small quantity of ultrapure water was added to the well of the device before the transport lid was fitted. This was to ensure that the disk remained wet until use.

The samplers were stored in ziplock bags at 4 °C until exposure. Triplicate Chemcatcher® samplers were deployed in the catchment streams and retrieved following the procedure described by Townsend et al. (2018). To ensure quality control, two field blanks were exposed to the air to account for any contaminants that accumulate in the Chemcatcher® sampler during transportation and handling during deployment and retrieval at the sampling sites. Three Fabrication blanks were also used to account for any background contamination by organic chemicals during preparation, laboratory storage, processing and analytical procedures. In a study by Townsend et al. (2018) spot water samples were used to ensure Chemcatcher® calibration. Results showed a good match between water sample results and those from Chemcatcher® derived data.

After removing from the catchment streams, the passive samplers were stored in a cooling box at 4 °C and transferred to the laboratory (T.E. Laboratories Ltd.), where the housing was cleaned and carefully disassembled. The receiving disk was eluted twice with 25 mL of ethyl acetate:formic acid solution (90:10). The two extraction solutions were combined and evaporated to dryness under a gentle stream of nitrogen in a fume hood. Herbicide residues in the extraction tube were re-dissolved in 1 mL of methanol and analysed using liquid chromatography tandem mass spectrometry (LC-MS/MS) (Cyfoeth Naturiol Cymru - Natural Resources Wales, UK). The analysis was carried out for acidic herbicides listed in Table 2. The minimum reporting values for studied acidic herbicides ranged between 0.005 and 0.01 $\mu\text{g L}^{-1}$.

2.4. Groundwater source drinking water sampling

A total of 51 private drinking water wells were sampled from the Grassland catchment and 44 wells from the Arable catchment. All samples were taken from a cold-water tap fed directly from the borehole. Each tap was run for a standard period of 5 min prior to sample collection

to purge the well and avoid the collection of stagnant water from within the well or plumbing system. During the purge period, routine field measurements were monitored for parameter (pH, conductivity and temperature) stabilisation. The sampling procedures and protocols used were based upon those outlined by the United States Geological Survey, USGS (2018). Sample-collection points were near the wellhead, ahead of where water enters pressure tanks, or treatment systems. Samples were taken in 1 L glass bottles and sent to Cyfoeth Naturiol Cymru - Laboratory Natural Resources Wales for the determination of acid herbicides via LC MS/MS.

2.5. Analytical methods

In the laboratory, a 1000 μL sample aliquot was transferred into a 2 mL silanised vial. Mass labelled internal standards (which are representative of the compounds being determined) were added to an aliquot of the preserved sample prior to analysis. Then 100 μL of sample was injected into a liquid chromatograph (Agilent 1260) which was interfaced to a triple quadrupole mass spectrometer (Agilent 6460). The mass spectrometer operated in negative ion atmospheric pressure electrospray ionisation (ESI) mode, using multiple reaction monitoring (MRM) to acquire data. The entire analytical system was automated. Quantification of target compounds was performed by using multi-level internal standard calibration. The analytes were separated on an Agilent (Zorbax) Eclipse Plus column (C18, 100 \times 201 mm, 3.5 μm particle size) maintained at 40 °C. The mobile phases were 0.1% acetic acid in ultra-high purity water (A) and acetonitrile (B) with the following linear-gradient programme. The elution gradient starting at 95% A and 5% B, was held for 0.3 min, and rose gradually to 100% B in 11.9 min, and was held for 1.8 min. After this systematic change, the mobile phase composition returned to its initial condition in 0.5 min, and this was held for 6.5 min. The total chromatography run time was 21 min with a constant flow rate of 0.4 mL min^{-1} . The spectrometer was equipped with an ESI Jet Stream source. Source parameters were optimized as follows: a capillary voltage of 3000 V for the negative ESI mode, source gas temperature was 300 °C with a flow of 5 L min^{-1} , nebuliser pressure of 45 psi, sheath gas temperature was 250 °C and

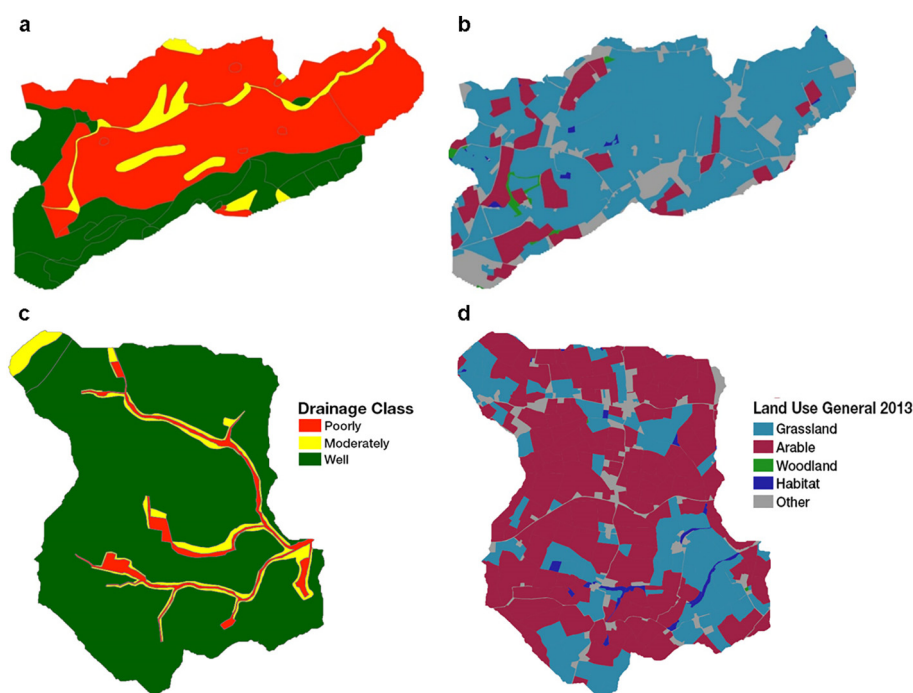


Fig. 2. a) Soil drainage class in the Grassland catchment, b) Land use in the Grassland catchment, c) Soil drainage class in the Arable catchment, and d) Land use in the Arable catchment.

sheath gas flow of 10 L min^{-1} . The retention times for studied compounds ranged between 2.14 and 10.75 min.

This analytical method was developed in house based on the *Standing Committee of Analysts (SCA) (2016)* blue book. The method is accredited to ISO17025 by UKAS and was validated to NS30 requirements. Analytical quality control (AQC) samples of known concentrations were run in duplicate with every batch of samples to ensure the reproducibility of the instrument. The method was also evaluated periodically using the LGC proficiency testing scheme Aquacheck.

2.6. Data analysis

Individual herbicide concentrations in surface water were calculated as total weighted average concentrations (TWA, ng L^{-1}) over the sampling interval/deployment period. These herbicide concentrations were then summed to calculate the total concentration (ng L^{-1}) of herbicides during the sampling interval/deployment period. Concentrations below the Limit of Quantification (LQ) were treated as 0 ng L^{-1} . The temporal concentration trend of herbicides in surface water was assessed by plotting individual herbicide concentrations against daily stream discharge

(Q , mm) and rainfall (mm) over the entire monitoring period in the two catchments. Individual herbicide loads (g) were calculated as the product of TWA and the sum of daily stream discharge, which were then summed to calculate the total herbicide load for the deployment interval. Daily stream discharge (mm) was calculated by dividing the daily stream flow (m^3) by the total area of the catchment (m^2). The sampled drinking water wells were divided into 10 groups in the *Grassland Catchment* and 9 groups in the *Arable Catchment*. The groupings of well clusters were based on the detection and concentrations of herbicides found within a 500 m radius.

3. Results and discussion

3.1. Hydrology

Total annual rainfall recorded during the year 2019 in the *Grassland* and *Arable* catchment was 1030 mm and 1110 mm, respectively. This was similar to the 10-year average annual rainfall (2009–2019) of 1037 mm and 1012 mm (Table 1). The rainfall distribution was similar between the catchments. While the catchments normally receive most

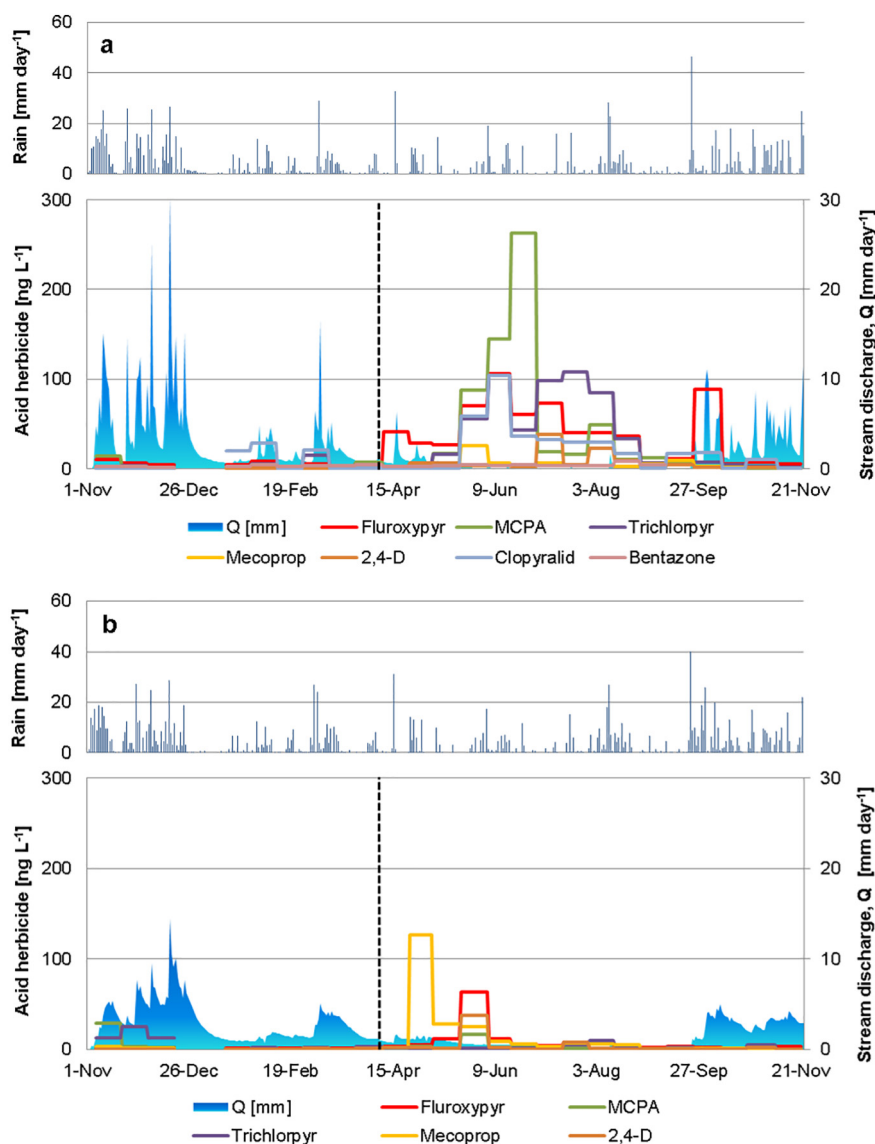


Fig. 3. Concentrations of detected herbicides (ng L^{-1}) in the stream, stream flow and rainfall (mm day^{-1}) at the outlets of a) the *Grassland Catchment* and b) the *Arable catchment* from November 2018 to November 2019. The vertical dashed line marks the average starting time of herbicide application in Ireland.

rain in October to December, there was more rain than normal in March and April 2019, with major rainfall events on 3rd and 5th of March and on 15th of April 2019 (Fig. 3). In April 2019 there was 88% more rain (105 mm) than the 10-year average (56 mm), coinciding with the time of year when herbicides are most frequently applied to grassland and arable crops. The two catchments also received rainfall between 45 and 51 mm on 8th and 9th of August 2019 (Fig. 3). Such rain events likely trigger an increase in overland flow resulting in incidental loss of applied herbicides causing contamination of surface waters. It is common practice to use more pesticides when the soil is not dry and when the vulnerability of crop disease and grassland weed growth is greatest (Rabiet et al., 2010).

3.2. Occurrence of herbicides in surface water

Of the 18 herbicides screened by the Chemcatchers®, MCPA, Fluroxypyr, Mecoprop, 2,4-D and Trichlorpyr were detected in variable concentrations throughout the study period in the river outlets of the two catchments (Fig. 3). Time weighted average concentrations of individual herbicides ranged from below the LQ to 262.9 ng L^{-1} in the *Grassland catchment* and from below the LQ to 127 ng L^{-1} in the *Arable catchment*. Bentazone was detected during all the sampling intervals in the *Grassland catchment* in concentrations ranging from 1.4 to 8.1 ng L^{-1} , while its concentrations were below LQ in the *Arable catchment*. Although Clopyralid was not detected in all the sampling intervals in the *Grassland catchment*, its concentrations ranged from 19.6 to 28.9 ng L^{-1} during mid-January to mid-March 2019 and from below

LQ to 103.7 ng L^{-1} between 22nd May and 21st August. In the *Arable catchment*, Clopyralid was only detected in the streams during November 2018 where its concentrations ranged between 16.9 and 21.1 ng L^{-1} and during the sampling intervals 22nd May to 6th June and 22nd October to 8th November with recorded concentrations of 25.1 and 13.3 ng L^{-1} respectively. Benazolin was detected in surface water between September and November 2019 with concentrations ranging from 8.4 to 13.2 ng L^{-1} in the *Grassland catchment* and from 5.5 to 7.2 in the *Arable catchment*. Dicamba was found only in the *Arable catchment* during one sampling interval between 8th and 21st November 2019 where its concentration was observed to be 12.6 ng L^{-1} . Concentrations of all the remaining herbicides were below the LQ in the two catchments.

The results indicate that in both catchments herbicides were present in the streams throughout the year, and there were large seasonal and temporal variations in their types and concentrations (Fig. 3). In both catchments the concentrations of herbicides were low during high flow conditions in winter (November to March). In April and May the herbicide concentrations started to increase which matched the timing of herbicide application in the area. This was followed by high herbicide concentrations during low flow conditions in June and July, and a steady decrease in August (Fig. 3). The time weighted average (TWA) of four herbicides in the *Grassland catchment* occasionally exceeded the legislative limit of 100 ng L^{-1} (MCPA = 262.9 ng L^{-1} , Trichlorpyr = 107.7 ng L^{-1} , Fluroxypyr = 106.0 ng L^{-1} and Clopyralid = 103.7 ng L^{-1}). In the *Arable catchment*, Mecoprop was the only herbicide that breached the legislative standards (TWA = 127 ng L^{-1}) at one sampling interval between 24th April to 7th May (Fig. 3).

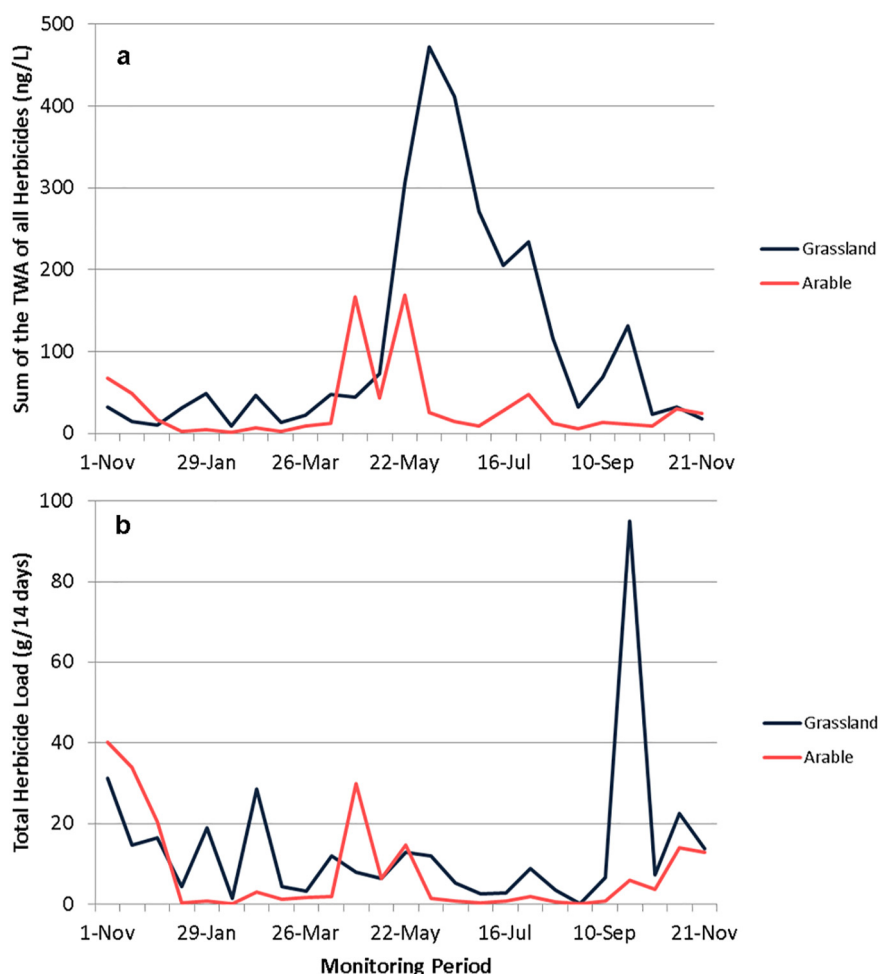


Fig. 4. Temporal variation in total herbicide a) concentration (ng L^{-1}) and b) load (g) in stream in the *Grassland* and *Arable catchments* from November 2018 to November 2019.

In both catchments, there were times when herbicide concentrations were highly variable over a short period of time. For example, in the *Grassland catchment*, MCPA and Fluroxypyr concentrations decreased from 14.0 and 10.5 ng L⁻¹ to 1.6 and 6.5 ng L⁻¹ respectively, while in the *Arable catchment*, MCPA concentrations decreased from 28.9 to 3.5 ng L⁻¹ between the two consecutive sampling intervals in November 2018. This variability in herbicide concentrations may be related to the hydrology of the two catchments. For instance, in November 2018, the *Grassland* and *Arable catchment* received a total rainfall of 243 and 230 mm respectively with several storm events. Such rainstorm events generate quick runoff, particularly in the poorly drained soils of the *Grassland catchment*, and also mobilise water content stored within the soil pore spaces and shallow water table via subsurface pathways as in the *Arable catchment*. This shift in soil hydrology was also likely to mobilise residue (i.e. not decomposed) herbicides stored in soils with variable quantities being transported to surface waters over relatively short periods of time.

Similarly, there was an observed sharp change in the concentrations of Clopyralid (below LQ to 58.4 to 103.7 to 35.8 ng L⁻¹), Fluroxypyr (27.0 to 70.4 to 106.0 to 60.3 ng L⁻¹), MCPA (0.9 to 17.1 to 87.6 to 144.9 to 262.9 to 18.9 ng L⁻¹) and Trichlorpyr (5.1 to 16.1 to 55.8 to 104.5 to 43.3 ng L⁻¹) between the consecutive sampling intervals during May and July. Similar behaviour was observed in the *Arable catchment* where there was a sharp increase in the concentrations of MCPA (0.9 to 16.8 ng L⁻¹), Fluroxypyr (12.1 to 63.0 ng L⁻¹) and 2,4-D (0.8 to 37.1 ng L⁻¹) between the two consecutive sampling intervals during May 2019. Mecoprop concentrations sharply increased from 1.8 to 127.0 ng L⁻¹ in the *Arable catchment* during April 2019. These sharp changes in the availability of herbicides in surface water during this time were likely associated to the timing of herbicide applications followed by large rainfall events. The total rainfall recorded during June and July in the *Grassland catchment* was 134 mm (with large events on 4th, 14th, 15th and 23rd June and 11 and 19th July) and in the *Arable catchment* 126 mm (with large events on 4th and 23rd June and 19th July). Soils were mostly dry and deficient in moisture content during this time of the year and so any rainfall could potentially trigger large volumes of infiltration excess surface run-off especially in poorly drained soils. This was reflected in large incidental losses of herbicides in the *Grassland catchment* in June and July (Fig. 3). Similarly, high concentrations of Mecoprop in the *Arable catchment* during the sampling interval between 24th April and 7th May were associated with the time of usage and rainfall events. During this time, the catchment received a total rainfall of 52 mm during the first seven days of deployment (with three main rainfall events). As the *Arable catchment* is characterised by well drained soils, it can be assumed that Mecoprop losses were predominantly via fast shallow subsurface pathways triggered by rainfall events soon after application. It was clear that hydrological conditions played a major role in the mobilisation and transport of herbicides from land to surface waters (Rabiet et al., 2010), and the contrasting controls on dominating flow pathways resulted in large variability in their concentrations.

The total herbicide concentrations ranged from 8.9 to 472.6 ng L⁻¹ in the *Grassland catchment* and 0.9 to 169.1 ng L⁻¹ in the *Arable catchment* during the sampling intervals throughout the monitoring period (Fig. 4a). The highest total herbicide concentration (472.6 ng L⁻¹) was observed during June in the *Grassland catchment* and this was the time when individual concentrations of MCPA, Trichlorpyr, Fluroxypyr and Clopyralid were in breach of legal standards in the surface water. The maximum total herbicide concentrations in the *Arable catchment* were observed between end of April and start of June 2019. As a note of caution, the TWA concentrations also probably masked much higher instantaneous herbicide concentrations during peak pollution periods and that were averaged into the overall deployment period estimates.

The fortnightly load of total herbicides in surface water leaving the catchment ranged from 0.2 to 85.4 g in the *Grassland catchment* and from 0.2 to 40.1 g in the *Arable catchment* during the monitored period

(Fig. 4b). The highest herbicide load of 85.4 g in the *Grassland catchment* was recorded between end of September and start of October, with 75% of this being from Fluroxypyr alone. The total load of herbicides in surface water in the *Grassland* and *Arable catchment* recorded during one complete year (between 6th November 2018 and 7th November 2019) was 310 and 175 g, respectively. Herbicide loads were higher in winter than summer in both catchments (Fig. 4b). This indicates that, even at low average herbicide concentrations, higher quantities of herbicides were present in surface water during high flow conditions. However, these estimated annual herbicide loads are comparatively low for these two catchments. For example, using a 7hourly MCPA concentration and discharge dataset in the River Derg in north-west Ireland, Morton et al. (2019) – see Fig. 4 in that paper) estimated a load of 9.3 kg over a 12 day period in June 2018 due in large part to incidental losses during storm events (Dr R. Cassidy, pers.comm).

Nevertheless, since hydrology explained much of the herbicide loss in the two study catchments, flow controls clearly played an important role and the relationship between total herbicide concentrations and water flow observed during passive monitoring in the outlets of the two catchments were clearly contrasting (Fig. 5). The passively sampled herbicide concentrations generally decreased with increased water flow in the *Grassland catchment* and in the *Arable catchment*, herbicide concentrations were not dependent on the stream flow. In these freely drained *Arable catchment* soils, herbicides were likely transported to surface water via below ground pathways where, for example, slow processes of water transfer through soil matrix such as drainage, subsurface runoff and exchanges with shallow water table (Müller et al., 2003; Rabiet et al., 2010) play an important role in the mobilisation of herbicides. The high herbicide concentrations during lower water flow in the *Grassland catchment* correspond to the timing of herbicide application in the area. Additionally, surface quickflow process resulted in

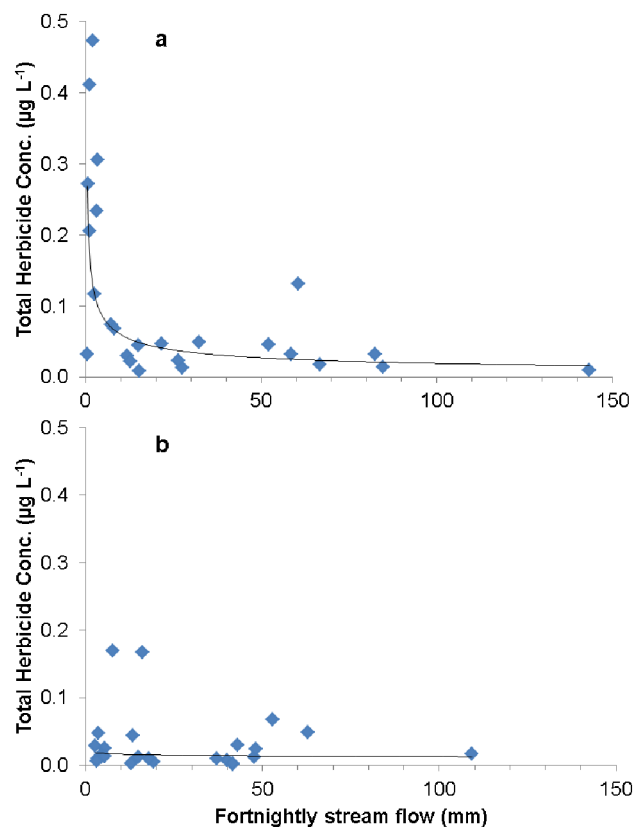


Fig. 5. Changes in total herbicide concentrations ($\mu\text{g L}^{-1}$) in response to stream flow (mm) in the a) *Grassland catchment* and b) *Arable catchment* from November 2018 to September 2019.

large fluxes of herbicide in surface water (albeit with lower concentrations).

Herbicides are mostly applied in the two catchments during spring (March to May) and prohibited from 15th October to 12th January as the soils are mostly saturated due to high seasonal rainfall. The herbicides present in the streams at times when they were not typically used indicated a rain triggered release of legacy herbicide (residue) stores in the soil, sediment and/or in ground water. This would typically be the case in soils and sediments rich in organic carbon and low in oxygen which inhibits the degradation of some herbicides (Morton et al., 2019). Importantly, this winter release of un-degraded herbicides was a higher flux than the incidental losses recorded in summer.

3.3. Occurrence of herbicides in source drinking water

Herbicides were detected in the well-sampled drinking water in six out of ten areas within the *Grassland catchment* and in four out of nine areas within the *Arable catchment* (Fig. 6). The most affected in the

Grassland catchment were areas 9, 8 and 10 with total herbicide concentrations of 299, 137.7 and 136.4 ng L⁻¹, respectively. This was followed by areas 1 and 3 where total herbicide concentrations were observed to be 90.6 and 89.2 ng L⁻¹ respectively. The lowest total herbicide concentrations of 1.7 ng L⁻¹ was found in area 5, while none of the herbicides were detected in areas 2, 4, 6 and 7. In the *Arable catchment*, comparatively low concentrations of herbicides were detected in different areas. The highest concentrations were detected in area 3 with 50.2 ng L⁻¹ and area 5 with 25.7 ng L⁻¹. Elsewhere, lower concentrations were found in areas 1 (5.0 ng L⁻¹) and 6 (7.6 ng L⁻¹). While the sum of herbicides concentrations was below the drinking water standards in all the areas, there were specific herbicides that exceeded the allowed limit of 100 ng L⁻¹ (Fig. 7).

In the *Grassland catchment* there were individual wells with high detections of Clopyralid (619 ng L⁻¹) and Trichlorpyr (650 ng L⁻¹), which highlighted a large variability in these herbicides and sometimes exceeding the legislation limit. In areas 1, 3, 8, 9 and 10 Clopyralid, Picloram, Benazolin, Fluroxypyr, Bentazone, 2,4-D, MCPA, Trichlorpyr,

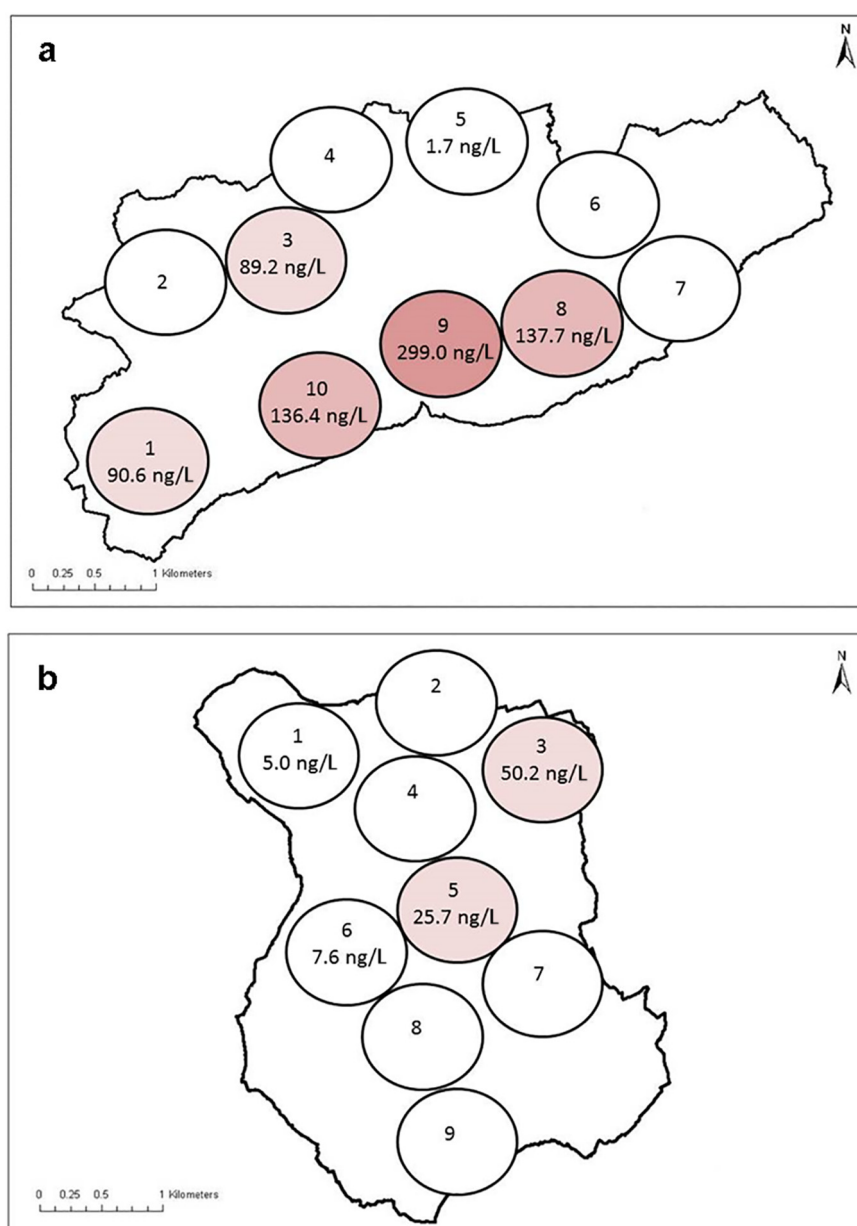


Fig. 6. Average sum of detected herbicide concentrations (ng L⁻¹) in drinking water for a) 10 clustered areas in the *Grassland catchment* and b) 9 clustered areas the *Arable catchment*.

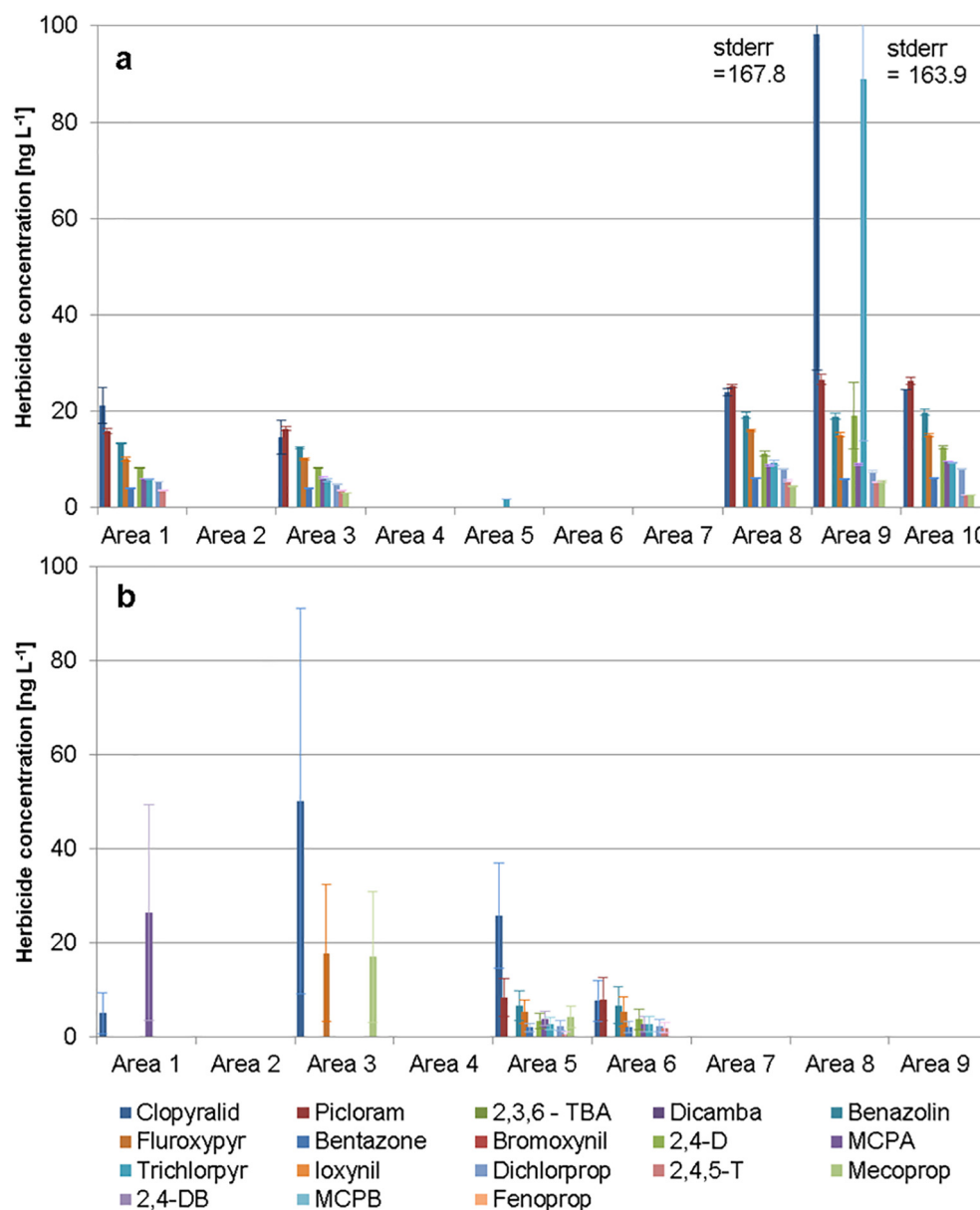


Fig. 7. Average herbicide concentrations and standard error (ng L^{-1}) in drinking water for 9–10 clustered areas in a) the *Grassland* catchment and b) the *Arable* catchment. Individual wells in Area 9 of the *Grassland* catchment largely exceeded the recommended drinking water limit for Clopyralid and Trichlorpyr.

Dichlorprop, 2,4,5-T and Mecoprop were detected. However, only in area 9 was the legislation limit exceeded. In the *Arable* catchment the distribution of compounds was slightly different. In area 1 Clopyralid and MCPA were detected, in area 3 Clopyralid, Fluroxypyr and Mecoprop were detected, in area 5 Clopyralid, Picloram, Benazolin, Fluroxypyr, Bentazone, 2,4-D, MCPA, Trichlorpyr, Dichlorprop, 2,4,5-T and Mecoprop were detected, and in area 6 was the same as area 5 with the exception of Mecoprop.

Although the *Grassland* catchment is dominated by poorly drained soils (Fig. 2a), detected herbicides were mostly associated with the well-drained soil found in the more elevated parts of the catchment where soluble herbicides could be leached to groundwater. In the *Arable* catchment the highest levels of herbicides were detected in the low lying areas adjacent to the stream. This may be explained by the catchment being dominated by relatively thin and well drained soils allowing for leaching of herbicides to the groundwater and flow accumulation near the river outlet due to relatively quick belowground pathways in the highly permeable weathered slate resting on the competent bedrock

(Mellander et al., 2014, 2015). The herbicides found in these areas were likely from recent crop applications.

In present study, herbicides were detected in 38% of 95 wells, and in 36% more than one herbicide was found. These results were similar to other studies of groundwater polluted by herbicides (Imran and Jain, 1998; Charles, 1989). Imran and Jain (1998) and Close and Humphries (2016) reported pesticides present in drinking water wells in Switzerland, Netherlands, Italy, Israel, Japan, Canada, Australia, USA and New Zealand. In New Zealand Close and Humphries (2016) found pesticides in 17% of 165 wells and two or more pesticides were found in 10% of the wells.

3.4. Implications for management

Measures to mitigate loss of herbicides to water need to be targeted and would benefit from being developed collaboratively with multiple stakeholders such as researchers, farmers, industry representatives, regulators and NGOs to increase measure acceptance and uptake

(Tournebize et al., 2012). Mitigation measures need to consider risky areas and risky times for the application of herbicides to avoid both incidental losses and the build-up of stores (Sandin et al., 2018; Quaglia et al., 2019). Such areas and times vary with different physical settings and landuse, and some efficient measures could be associated to behavioural changes in the handling of herbicides (Damalas and Koutroubas, 2018). Research based knowledge transfer would play an important role (Owa, 2013). Farm advisors, consultants, rural professionals, multi actor discussion groups and topical events would contribute to an effective knowledge transfer. Regulations may also be revised with compliance to be effectively monitored.

4. Conclusions

In the two monitored catchments it was found that, despite not being areas recognised for problems associated with herbicides pollution in water (indeed, passively sampled mass loads leaving the catchments were comparatively low), many of the monitored herbicides were present in both surface and groundwater, and in some cases well above the recommendations for drinking water. An important finding was related to the larger winter fluxes of herbicides in surface water, compared to incidental losses during periods normally associated with application. This suggests persistence of primary chemical residues in soil and sub-surface environments and restricted degradation.

These herbicide losses to surface water were source limited and strongly influenced and driven by the physical and hydrological conditions of the two catchments. High concentrations of herbicides in surface water during summer were attributed to the timing of herbicide usage, low flow and lack of dilution and this was when the individual concentrations of MCPA, Trichlorpyr, Fluroxypyr, Clopyralid and Mecoprop were in excess of EU legislative limit of $0.1 \mu\text{g L}^{-1}$, mainly in the *Grassland catchment*. The presence of herbicides in variable concentrations was also demonstrated in drinking water wells in different areas across the two catchments. The individual concentrations of Clopyralid (up to 619 ng L^{-1}) and Trichlorpyr (up to 650 ng L^{-1}) were in excess of drinking water quality standards in the well-drained upland soils in the *Grassland catchment*.

These results highlight gaps in our understanding of water quality dynamics and carry important consequences for developing collaborative mitigation strategies to reduce herbicide losses to water. Using this multi-dimensional and whole catchment approach, further studies should be conducted in different catchment typologies and in smaller sub-catchments to better identify the temporal and spatial variability of drivers and controls for loss of pesticides to water.

CRedit authorship contribution statement

Majid Ali Khan: Conceptualization, Investigation, Writing - original draft. **Fabiola Barros Costa:** Conceptualization, Investigation, Writing - original draft. **Owen Fenton:** Conceptualization, Writing - review & editing, Supervision. **Phil Jordan:** Conceptualization, Writing - review & editing, Supervision. **Chris Fennell:** Methodology, Investigation. **Per-Erik Mellander:** Conceptualization, Methodology, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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